INSULATED NANOSCOPIC PATHWAYS, COMPOSITIONS AND DEVICES OF THE SAME

Related Applications

5   This application claims priority to U.S. Provisional Patent Application Serial No. 60/180,357, filed 02/04/00.

Field of Invention

The present invention provides articles, devices, compositions and methods involving

10   conduction pathways of nanoscopic thicknesses. Applications for such devices include sensors for a variety of analytes.

Background of the Invention

There is a considerable interest in the preparation and use of conducting pathways of

15   the nanoscopic scale as the need for miniaturization and heightened signal sensitivity increases. A class of such conducting pathways include conjugated polymers comprising organic and/or inorganic components, e.g. "molecular wires". Typically, these molecular wire polymers will be incorporated in devices as a film having an extensive intertwined array of individual conducting pathways. Each individual pathway is provided by a polymer chain,

20   or a nanoscopic aggregate of polymer chains.

FIG. 22 shows a schematic diagram of a prior art device 100. Device 100 comprises a polymer film 105 deposited on substrate 101 between electrodes 102 and 103, in which film 105 is capable of conducting charge. An electrical circuit 104 capable of determining the resistance with voltmeter (or ammeter) 107 completes device 100. Polymer film 105

25   comprises a plurality of individual polymer chains 106 (drawn as straight lines for illustrative purposes – in reality, the chains are often intertwined). Because no individual polymer chain extends between the electrode, charge conduction must occur through film 105 by charge "hopping" between individual chains (e.g. between chains 106a and 106b). A disadvantage in many films, however, is that the presence of bound guests 108, which may impede charge

30   conduction throughout film 105, is not capable of producing as large of chemical signal as is optimal due the presence of a continuum of parallel pathways. In such materials the charge

carriers responsible for the charge conduction can taken an alternative path that avoids the impediments introduced by the bound guests.

One application for nanoscopic pathways is a sensor, particularly for sensing specific molecules. Such sensors include receptor sites to bind analytes via molecular recognition.

5   FIG. 23 shows a schematic of a plurality of isolated receptor molecules 120, each comprising a receptor site 124. Prior to binding analyte 126, receptor molecule 120 has a particular "state" schematically represented by open oval 122, which can define an oxidation state, conformation state, etc. In order to detect a binding event, the sensor relies on a change in the state upon binding an analyte. FIG. 23 schematically shows this change in state with

10   receptor molecule 130 which is bound to analyte 126 and has a change in state depicted by blackened oval 123. Receptor molecules 120 which do not bind analyte 126 remain in state 122. FIG. 23 depicts a binding event as an equilibrium between a concentration of bound receptors and receptors prior to binding. Sensitivity of the device is thus determined by the equilibrium constant $K_{(eq)}$ = [Bound receptor]/([Unbound receptor][Analyte]).

15   The use of conducting polymer films in sensor applications has the potential to increase the sensitivity. FIG. 24 shows a schematic of a polymer film 130 comprising a plurality of individual polymer chains 132. Film 130 spans a dimension 131, which is the dimension between electrodes if incorporated into a device.

FIG. 25 shows a schematic expansion of individual chain 132, in which receptors 142

20   are incorporated into chain 132 and interspersed between conducting polymer regions 140, i.e. receptors 142 are wired in series. Preferably, the entire chain comprising regions 140 and 142 comprise a continuous conducting pathway. Each receptor has a site 144 with an initial state depicted by open oval 143. Upon binding analyte 146, the state 146 of each receptor site 142 is affected due to the electronic communication existing between each receptor site

25   142. The result is a large signal amplification. Only a fractional occupancy is required to achieve a collective signal response.

Despite such recent improvements, there still exists a need to improve the signal amplification for sensors requiring even heightened sensitivity. There also exists a need to develop new nanoscopic materials and materials systems.

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Summary of the Invention

One aspect of the invention provides an article comprising a nanoscopic pathway having a conductivity. A dielectric insulates the nanoscopic pathway. A nanoscopic switch in electronic communication with the nanoscopic pathway is capable of altering the conductivity of the nanoscopic pathway.

Another aspect of the present invention provides a composition comprising a nanoscopic pathway and a polymer isolating the nanoscopic pathway. The nanoscopic pathway has a resistance of less than 10^{-4} times a resistance of the polymer.

Another aspect of the present invention provides a method for altering conductivity, comprising the step of providing an article comprising a nanoscopic pathway having a conductivity. The method further comprises the steps of insulating the nanoscopic pathway; and activating a nanoscopic switch positioned in the article.

Another aspect of the present invention provides a method for detecting the presence of a analyte, comprising the step of providing an article comprising a nanoscopic pathway having a conductivity. The method further comprises the steps of insulating the nanoscopic pathway, and activating detection sites positioned in the article.

Another aspect of the present invention provides a method for amplifying conductivity, comprising the step of providing an article comprising a nanoscopic pathway. The method further comprises the steps of positioning a plurality of nanoscopic switches in the article, and activating a number of the plurality of nanoscopic switches, the number being greater than a percolation threshold.

Another aspect of the present invention provides a method for reducing conductivity, comprising the step of providing an article comprising a nanoscopic pathway. The method further comprises the steps of positioning a plurality of nanoscopic switches in the article, and deactivating a number of the plurality of nanoscopic switches, the number being less than a percolation threshold.

Another aspect of the present invention provides a method for detecting the presence of an analyte, comprising the step of providing an article comprising a nanoscopic pathway. The method further comprises the steps of positioning a plurality of nanoscopic switches along the nanoscopic pathway, and activating a number of the plurality of nanoscopic switches, the number being greater than a percolation threshold.

Another aspect of the present invention provides a method for detecting the presence of an analyte, comprising the step of providing an article comprising a nanoscopic pathway. The method further comprises the steps of positioning a plurality of nanoscopic switches along the nanoscopic pathway, and deactivating a number of the plurality of nanoscopic

5   switches, the number being less than a percolation threshold.

Another aspect of the present invention provides a method for synthesizing a conducting polymer comprising the step of providing a monomer having a first and second polymerization site. The method further comprises the steps of polymerizing the monomer at the first site to produce a first polymer, and polymerizing the monomer at the second site to

10   produce a second polymer, the second polymer isolating the first polymer.

Another aspect of the present invention provides a block co-polymer, comprising blocks of a conducting material and blocks of a dielectric material. The blocks are arranged such that the blocks of the conducting material form a nanoscopic pathway insulated by blocks of the dielectric material.

15   Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For purposes of clarity, not every component is

20   labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

Brief Description of the Drawings

25   FIG. 1 shows a schematic cross-section of an article having a nanoscopic pathway isolated by a dielectric and including nanoscopic switches;

FIG. 2A shows a schematic cross-section of a multi-stranded polymer having a central conducting polymer strand isolated by multiple dielectric polymer strands, the multi-stranded polymer including nanoscopic switches;

30   FIG. 2B shows a central conducting polymer isolated by a single dielectric polymer;

FIG. 3 schematically illustrates the aggregation of a nanoscopic pathway (a) to provide a larger nanoscopic pathway comprising an interconnected series of nanoscopic pathways (b);

FIG. 4A shows a schematic cross-section of a percolation network comprising conducting links and dielectric links having nanoscopic switches;

FIG. 4B shows the percolation network of FIG. 4a at or above the percolation threshold;

FIG. 5 schematically shows blocks A and B (a), a resulting block copolymer (b) and a resulting microphase separation of a film of a block copolymer (c) comprising conducting blocks A isolated by dielectric blocks B;

FIG. 6A shows two types of monomers that can be used in a block copolymer of the present invention;

FIG. 6B shows two types of monomers that can be used in a block copolymer of the present invention;

FIG. 7 shows two types of monomers that can be used in a block copolymer of the present invention;

FIG. 8 shows two types of monomers that can be used in a block copolymer of the present invention;

FIG. 9 shows examples of block polymers that can bind semiconductor nanoparticles;

FIG. 10 shows a scheme for mixing 62, 63, and Cu^{1+} or Zn^{2+} ions to produce metallorotaxane monomers 60 and 61, and subsequent polymerization;

FIG. 11 shows cyclic voltammograms of 60, poly1, and poly1-L on interdigitated microelectrodes with a spacing of 5 μm between adjacent electrodes (0.1M (nBu$_4$N)PF$_6$ in CH$_2$Cl$_2$ at a sweep rate of 100 mVs^{-1}). a: A film of poly1 in fresh, monomer-free electrolyte. b: The first electropolymerization to grow films of poly1 after 1, 20, 40, and 60 potential cycles. c: The first scan (solid line) and second scan (dashed line) of the same film when swept to 1.0 V vs. Fc/Fc$^+$. The first scan shows the large irreversible oxidation to form poly1-L;

FIG. 12 shows solid lines: cyclic voltammograms of poly1-L (a), poly2-L (b), and poly4 (c), on 5 μm interdigitated microelectrodes (0.1 M(nBu$_4$N)PF$_6$ in CH$_2$Cl$_2$ at a sweep rate of 100 mVs^{-1}). Dashed lines: plots of the in situ conductivity versus applied oxidation

potential of the same films at a sweep rate of 5 mVs^{-1} with a 40 mV offset potential between adjacent electrodes;

FIG. 13 shows a schematic representation of the participation of the Cu ion in the nanoscopic pathway;

FIG. 14 shows a schematic representation of the synthesis of iptycene-containing phthalocyanine monomers: (a) 2 equiv of Br$_2$, CHCl$_3$ rt (87%); (b) 4 equiv of Na$_2$S$_2$O$_4$, 1:1 Et$_2$O:H$_2$O, rt (90%); (c) 5 equiv of K$_2$CO$_3$, 8 equiv of (CH$_3$)$_2$CHBr, DMF, 60°C, 3 d (93%); (d) 6 equiv of CuCN, DMF, 140°C, 3 d (71%): (3) cat. Na, NH$_3$ (g), ethylene glycol, 140°C, 5 h (87%); (f) 4-iodophthalonirile, Mg(OBu)$_2$, BuOH, reflux, 1 d; (g) M(acac)$_2$, THF, reflux, 1 d; (h) Bu$_3$EnEDOT, PdCl$_2$(PPh$_3$)$_2$, DMF, 60°C, 1 d;

FIG. 15 shows cyclic voltammograms (solid lines) and conductivity profiles (dashed liens) of (a) poly(9-Co) and (b) poly(9-Ni) in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$ on 2 μm interdigitated microelectrodes. Sweep rates are 100 mV/s for cyclic voltammograms and 5 mV/s with a 40 mV offset potential for conductivity measurement;

FIG. 16 shows cyclic voltammogram (solid line) and conductivity profile (dashed line) of poly(8-Co) in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$ on 2 μm interdigitated microelectrodes. Sweep rates and offset potentials were the same as in FIG. 15;

FIG. 17 shows cyclization of α-linked and β-linked species;

FIG. 18 shows electropolymerization (a) of the monomer: The dashed line is the first sweep and the increasing current with successive sweeps indicates that polymerization occurs; the cyclic voltammetric behavior of the thin film (b) on a 2 mm^2 platinum button electrode shows reversible electrochemical behavior, (scan rates were 100m V/s);

FIG. 19 shows examples of α-linked and β-linked tetrathienyl monomers;

FIG. 20 shows more monomers and polymers of the present invention;

FIG. 21 shows space-filling model of 60 (a) and an octamer of poly1-L (b);

FIG. 22 shows a schematic of a prior art device incorporating a polymer film capable of conducting charge;

FIG. 23 shows a schematic of an equilibrium between a plurality of isolated, unbound receptors and a plurality of receptors after being exposed to an analyte;

FIG. 24 shows a schematic of a polymer film capable of conducting charge comprising a plurality of individual polymer chains;

FIG. 25 shows a schematic of an expanded portion of a polymer chain of FIG. 24, where the polymer chain incorporates receptors for binding an analyte in equilibrium with a chain after exposure to an analyte; and

FIG. 26 shows a schematic of an idealized single molecule molecular wire extending the entire length between electrodes.

Detailed Description

The present invention features articles, devices, compositions and methods for conducting electronic charge having applications in sensors and microelectronic components. The present invention provides advantageous features over the prior art from enhanced conduction properties and analyte detection sensitivity due to insulation of a conducting nanoscopic pathway. Such articles, devices and compositions have a number of variables that can be tailored to a desired application.

One aspect of the invention provides an article comprising a nanoscopic pathway isolated by a dielectric. In one embodiment, the nanoscopic pathway is a medium for the conduction of electronic charge. "Nanoscopic" refers to a minimum dimension of the pathway, e.g. a mean diameter or a thickness of the pathway. In one embodiment, the nanoscopic pathway has a minimum dimension of less than about 20 nm, more preferably less than about 10 nm. The minimum dimension can be as small as a thickness of a single molecule, such as a minimum thickness of benzene. In one embodiment, the nanoscopic pathway has at least one length of at least about 0.05 μm, more preferably at least about 0.1 μm. Typically, this length is the length over which conduction occurs. The pathway can be a singular pathway or can include branched pathways.

The nanoscopic pathway can be an organic group, an organometallic compound, a coordination compound, a salt, a nanoparticle, a carbon nanotube, a biological species and combinations thereof. In one embodiment, the nanoscopic pathway can be provided by a molecular system (e.g. an organic or organometallic group) having a bonding arrangement which affords delocalization of electronic charge extending throughout a portion or entire length of the molecule. Thus, the nanoscopic pathway can have a length equal to the length of the molecule. In another embodiment, the nanoscopic pathway can comprise a series of interconnected nanoscopic pathways, and the length of the pathway is equal to a total length of the interconnected series of pathways. Examples of organic groups include polyaniline,

polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a

conjugated ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene),

poly(arylene ethynylene), the corresponding monomers, corresponding oligomers and organic

and transition metal derivatives thereof. Typical organometallic or coordination compounds

5   in a nanoscopic pathway include metals capable of delocalizing charge through bound

ligands. A variety of such compounds are known in the art. Silicon nanowires can also be

contemplated for use in a nanoscopic pathway.

In one embodiment, electronic charge can occur via charge transfer (electron

"hopping") between redox-active centers. "Redox-active" refers to a metallic, organic,

10   organometallic or metal ion species capable of accepting or donating electronic charge. The

charge transfer need not necessarily occur between two species having orbital overlap, and

can occur via a long range charge transfer mechanism. Charge transfer can include a transfer

of negative charge (e.g. an electron) or positive charge (e.g. a hole). For example, a

nanoscopic pathway can be provided from a collection of nanoparticles, i.e. particles having

15   at least one dimension less than about 1 μm which are arranged in electronic communication

with each other. The particles are capable of conducting electronic charge either via a charge

transfer mechanism or even through physical contact between the particles. In yet another

embodiment, the nanoscopic pathway can involve a combination of redox-active species in

conjunction with a conjugated pathway. In still another embodiment the nanoscopic pathway

20   can comprise species with metallic properties (e.g. having a conducting mechanism similar to

a metallic wire), for example species that do not have localized redox centers and hopping

conduction.

FIG. 26 shows an idealized diagram of a device having a molecular wire polymer

incorporating receptor sites, in which the molecular wire comprises a nanoscopic pathway

25   (e.g. poly(thiophene) or poly(pyrrole)) extending between two electrodes, allowing the

resistance to be measured. The distance between the electrodes defines the path length of the

nanoscopic pathway. In FIG. 26, device 150 comprises film 155 of a molecular wire polymer

deposited on substrate 151 between electrodes 152 and 153. An electrical circuit 154 capable

of determining the resistance with voltmeter (or ammeter) 157 completes device 150. Film

30   155 comprises receptor sites 156a-e interspersed between conjugated chains 158. Site 156d

is shown as bound to analyte 159. Energy along the nanoscopic pathway, depicted as line

160, increases as shown in the direction of the arrow adjacent the label "E". Binding of

analyte 159 by receptor 156d adds resistance to the wire, as schematically indicated by energy 160.

FIG. 26 helps illustrate advantages of an insulated nanoscopic pathway. Besides the ability to measure resistivity precisely with inexpensive electronics, it can be seen that a large amount of charge can migrate along the wire while the analyte is modifying the migration, thereby allowing a single analyte binding event to affect the migration of many electrons.

Although an ideal, the device of FIG. 26 in reality presents practical synthetic problems, including the fact that such single molecules do not retain their shape (i.e. not shape persistent) upon undergoing various chemical or electronic processes. Moreover, many molecules are not easily manipulated to provide the single pathway.

A feature of the present invention provides a nanoscopic pathway comprised of a plurality of nanoscopic wires are interrupted by one or more nanoscopic switches. The switches, when turned "on" can produce a continuous pathway extending through the plurality of nanoscopic wires, as connected by the intermittent switches, as described in more detail below.

In one embodiment, the nanoscopic pathways produce a material with a bulk conductivity of at least about 10^{-9} S•cm^{-1}, more preferably at least about preferably at least about 10^{-4} S•cm^{-1}, more preferably at least about 10^{-2} S•cm^{-1}, more preferably at least about 1 S•cm^{-1}, more preferably at least about 10^2 S•cm^{-1}, more preferably at least about 10^3 S•cm^{-1}, and even more preferably at least about 10^4 S•cm^{-1}. In one embodiment, at least a portion of the pathway has an intrinsic conductivity of the previously mentioned values. "Intrinsic conductivity" refers to a conductivity of the pathway at a resting state of an article or device incorporating the pathway, i.e. a conductivity that is present in the absence of an applied energy.

In one embodiment, a dielectric isolates the nanoscopic pathway. The dielectric can serve to isolate the pathway from contacting external substances. The dielectric can serve to electrically isolate (i.e. insulate) the pathway from other conduction pathways. In one embodiment, the dielectric has a resistivity of greater than about 10^8 ohm•cm. In one embodiment, the nanoscopic pathway has a resistance less than 10^{-4} times a resistance of the dielectric. Examples of dielectric materials include a molecular species including a polymer, a ceramic, a solvent, a vacuum, a gas, a liquid crystal phase, a microphase-separated block copolymer structure and combinations thereof.

In one embodiment, the article includes a nanoscopic switch. The article can have one nanoscopic switch per nanoscopic pathway, or a plurality of switches per nanoscopic pathway. The switch is a chemical or biological species capable of altering the conductivity of the nanoscopic pathway. The nanoscopic switch can be positioned anywhere in the article,

5   e.g. in the nanoscopic pathway, in the dielectric, along an interface of the dielectric and the nanoscopic pathway. "Altering" can involve either reducing or increasing the conductivity of the nanoscopic pathway. "Altering" can also involve completely shutting down the conduction, or turning the conduction "on" from an initially "off" state. Thus, the nanoscopic switch can mediate charge transfer (or conduction) through the pathway. In one embodiment,

10   the switch is redox-active, allowing it to participate in charge transfer, oxidation or reduction processes.

       In one embodiment, the nanoscopic switch is redox active. In one embodiment, the nanoscopic switch is capable of mediating electronic charge via a tunneling mechanism. In the situation where a material exhibits high conductivity, electronic charge can travel through

15   a pathway while experiencing relatively low energy barriers. "Tunneling" refers to a transfer of charge through a region having a high energy barrier.

       In one embodiment, the nanoscopic switch is capable of mediating charge via a chemical reaction. For example, the addition or removal of charge from a nanoscopic switch can result in the loss, formation, displacement or transfer of a chemical bond.

20   One embodiment of an article of the present invention is shown schematically in FIG. 1. FIG. 1 shows a cross-section of article 2 having a nanoscopic pathway 4 having a minimum dimension 5. Pathway 4 can comprise one continuous molecule or an interconnected series of molecules and/or nanoparticles. Nanoscopic pathway 4 is isolated by a dielectric 6. Dielectric 6 has a high resistance, and can be a vacuum, a gas, a liquid or a

25   solid material. Nanoscopic switches 8 can be positioned anywhere in the article so long as it serves to alter the conductivity of nanoscopic pathway 4. The various positions of nanoscopic switches 8 shown in FIG. 1 illustrates at least some of the possible positions of the nanoscopic switch in the article, and is not meant to indicate that the article must possess nanoscopic switches in all these positions. If desired, the article can include a plurality of

30   more than one type of nanoscopic switches in any position.

       In one embodiment, the nanoscopic switch operates by a change in conformation. Typically, a significant portion of the switch comprises an organic group capable of changing

conformation upon charge transfer. Examples of such compounds can be found in a paper entitled "A Three-Pole Supramolecular Switch" by P.R. Ashton et al., (*J. Am. Chem. Soc.* **1999**, *121*, 3951-3957), which is herein incorporated by reference in its entirety.

In the embodiment where the nanoscopic pathway comprises an organic group, the nanoscopic pathway can be provided by a molecular species having extended conjugation. Extended conjugation results from a series of chemical bonds having mobile π-electrons which can delocalize throughout a portion of the molecule or throughout the entire molecule. Where the nanoscopic pathway comprises an organometallic or coordination compound, the metal ion by virtue of s, p, d or f orbitals or mixtures thereof, provides a mechanism to delocalize charge, and this delocalization can occur with or without an organic group capable of participating in conjugation. Examples of nanoscopic pathways comprising an organic component include a conducting polymer such as those selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a conjugated ladder polymer (i.e. a polymer which requires the breaking of at least two bonds to break the chain), polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene). Of course, organic, organometallic or inorganic derivatives of the conducting polymer, and combinations of these derivatives are meant to be encompassed by the present invention, as known by one of ordinary skill in the art.

One example of an article of the present invention involves a multi-stranded polymer, as schematically shown in FIG. 2. FIG. 2A shows a cross-section of article 10 having a central conducting polymer strand 14 (schematically illustrated as a line) which functions as the nanoscopic pathway and at least one outer strand 16 (schematically illustrated as a line) which isolates the conducting polymer. For example, FIG. 2A shows at least two outer strands 16 in parallel arrangement with conducting polymer 14. FIG. 2B shows one outer strand 16 twisted in substantially helical formation around a conducting polymer 14. The arrangements of outer strands 16 in FIGs. 2A and 2B serve to isolate the conducting polymer from contacting any external entities. Outer strands 16 can be either a straight-chain polymer or branched, so long as it can isolate conducting polymer 14.

FIG. 3 schematically illustrates the aggregation of nanoscopic pathway to provide a larger nanoscopic pathway comprising an interconnected series of nanoscopic pathways. FIG. 3(a) illustrates a double-stranded polymer 20 having a nanoscopic pathway 24 comprising a first polymer and a dielectric comprising a second polymer 26. The first and

second polymers can be attached by attachment 25 which can comprise a chemical bond, or an intermediary chemical species (e.g. an organic group, a metal ion, a metal ion complex) or biological species. Nanoscopic switches 28 can be interspersed throughout the first polymer 24. Alternatively, attachment 25 can comprise a nanoscopic switch. FIG. 3(b) illustrates an

5   aggregate of double-stranded polymers 20. Preferably the aggregate is anisotropic in which the nanoscopic pathways have substantially the same orientation. The aggregate does not necessarily have to provide a linear pathway and can be curved, as demonstrated by double-stranded polymer 20. The aggregate can comprise nanoparticles or any article comprising a dielectric and nanoscopic pathway, as schematically illustrated in FIGs. 1 and 2.

10   In one embodiment, nanoparticles making up the nanoscopic pathway have anisotropic character, i.e. have an aspect ratio of greater than 5. In another embodiment, nanoparticles include nanotubes, metal clusters, semiconductor clusters, colloids and fibers. A minimum dimension of these particles can be that of the nanoscopic pathway, i.e. less than about 20 nm and preferably less than about 10 nm.

15   Nanotubes can be composed of sp^2 carbon atoms bonded exclusively to each other and arranged to enclose a hollow cavity. Carbon nanotubes are known to have conductivity properties. Other examples of nanotubes include metallized nanotubes, which comprise a metal coating over an organic substance. For example, a biological species (e.g. a lipid, a virus such as tobacco mosaic virus) or a chemical species (e.g. a surfactant) can provide a

20   template for metallization, i.e. a process for depositing a metal coating on a template. Thus, a thin metal coating in the shape of a hollow vessel, such as a tubule, can be formed having dimensions of less than about 20 nm, or any dimension sufficient to provide a nanoscopic pathway having dimensions as described herein. Examples of such metallization are described in Schnur, Science Vol. 262(5140), p. 1669-1676 (1993) or Chow et al., Materials

25   Science and Engineering A, Vol., 158(1), p. 1-6 (1992), each of which are incorporated herein by reference in its entirety.

Metal clusters and colloids comprise aggregates of metal atoms, such as gold, copper and silver. A typical minimum dimension of a cluster or colloid is about 2 nm. Colloids are typically dispersed in a second, host phase. In addition, a collection of colloids can adhere to

30   each other to produce colloidal aggregates. Semiconductor clusters typically comprise binary inorganic compounds such as metal halides, metal oxides, metal sulfides, metal chalcogenides, and III-V semiconductors. Examples include CdO, CdS, CdSe, CdTe, ZnO,

ZnS, ZnSe, PbS, PbSe, PbTe, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb and compositional mixtures thereof. Examples of fibers (nanofibrils) include graphite fibers, semiconductor nanowires and aggregated conducting polymers.

In one embodiment, the fibers forming a nanoscopic pathway can be formed by molecular processing. For example, a plurality of aligned nanoscopic pathways can be deposited on a substrate via a Langmuir-Blodgett process, in which polymers having a polar end ("head") and a non-polar end ("tail") are adsorbed onto a substrate as dictated by the substrate's affinity for polar or non-polar entities. In one embodiment, the polymers include π-electrons (e.g. in a double bond, a triple bond or an aromatic group such as a benzene ring). The π-electrons of one polymer can interact with the π-electrons in another polymer in a phenomenon known as "π-stacking" to form π-stacked aggregates. Such π-stacking can provide a nanoscopic pathway for conduction of charge. An example of such nanoscopic pathways is described in Kim et al., Macromolecules, Vol. 32, p. 1500-1507 (1999), which is herein incorporated in its entirety.

An example of electropolymerization of pyrrole to give fibers positioned between two electrodes is described in Curtis et al., Polymer Preprints, Vol. 35 p. 331 (March, 1995). In one embodiment, the fibers can be grown on a dielectric substrate.

In one embodiment, the dielectric is a polymer. Examples include polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, cellulose proteins and derivatives thereof. Other polymers that can function as a dielectric are readily known to those of ordinary skill in the art. The dielectric polymer can be a gel, such as a hydrogel, examples of which are compositions containing poly(acrylic acid), poly(vinyl alcohol), and poly(ethylene oxide).

The dielectric can be a ceramic. Ceramics typically comprise metal oxides, metal nitrides, mixed metal oxides or mixed metal nitrides. In one embodiment, the ceramic is a silicate, or includes silicate groups e.g. SiO_2. In another embodiment, the silicate is a porous silicate such as MCM41 as described by Beck et. al. in the Journal of the American Chemical Society 114, 10834-10843 (1992). In one embodiment, the dielectric can be a solvent such as water, or an organic solvent. The solvent can be a combination of two or more solvents. In one embodiment, the dielectric is a gas, and preferably an inert gas such as helium, neon, argon, nitrogen, etc. In one embodiment, the dielectric is a liquid crystal phase. The liquid

crystal phase can be a lyotopic liquid crystal (e.g. sodium dodecylsulfate, a phospholipid membrane), which requires the addition of solvent to provide anisotropic orientation of the liquid crystals. The liquid crystal phase can be thermotropic, as displayed by, for example, 5CB (pentyl substituted cyanobiphenyl). The liquid crystalline phases can further be used

5   align the nanoscopic pathways to create optimal isolation and positioning of the switching elements.

In one embodiment, the nanoscopic switch and the nanoscopic pathway are capable of being redox-matched. "Redox-matched" refers to a situation where a difference in redox potentials between the nanoscopic pathway and the nanoscopic switch is minimized. In one

10   embodiment, the nanoscopic switch and nanoscopic pathway are each redox-active. A "redox potential" refers to an electrochemical potential required to effect charge transfer either to and from the redox-active components. When at least one component is conducting and exhibits a maximum conductivity at a particular redox-potential or redox-potential range, redox-matching allows an optimal mixing of electronic states of the conductor with electronic

15   states of its redox-matched partner, thereby enhancing electronic communication. The enhanced electronic communication can increase conductivity. In one embodiment, redox-matching can be achieved by altering a chemical property of either the nanoscopic switch or the nanoscopic pathway. For example, the nanoscopic switch and the pathway may undergo redox-chemistry at different electrochemical potential ranges. In an examples where the

20   nanoscopic switch comprises a coordination compound, altering the electron-donating properties of the ligand can shift the electrochemical potential range to match that of the nanoscopic pathway. In another example, the nanoscopic pathway can be derivatized with groups having electron-poor or electron-rich properties, such that the pathway has an electrochemical potential range matching that of the nanoscopic switches. Redox-matching

25   and examples of redox-matching is discussed further in co-pending U.S. Application Ser. No. 09/201,743, to Swager et al. entitled "Conducting Polymer Transition Metal Hybrid Materials and Sensors," filed December 1, 1998, which is incorporated herein by reference.

In one embodiment, the a nanoscopic pathway is a conductor within a defined electrochemical potential range. This type of pathway requires an input of electrochemical

30   energy to afford conduction. In one embodiment, this pathway is non-conducting outside of this defined electrochemical range. In one embodiment, the nanoscopic pathway comprises a first nanoscopic pathway and is a conductor within a first electrochemical potential range.

The first nanoscopic pathway can be isolated by a second nanoscopic pathway. The first nanoscopic pathway can have a resistance of less than 10^{-4} times a resistance of the second nanoscopic pathway, i.e., the second nanoscopic pathway is a dielectric.

In one embodiment, the second nanoscopic pathway is an insulator within a particular electrochemical potential range and is capable of being a conducting at a second electrochemical potential range. In one embodiment, the second electrochemical potential range is greater than the first electrochemical potential range.

In one embodiment, either the nanoscopic switch, the nanoscopic pathway or the dielectric comprises a biological species. In one embodiment, DNA can act as a nanoscopic pathway. The capability of DNA to provide a pathway for conduction (either by hole transfer, or long range charge transfer) has been described in Holmlin et al., J. Am. Chem. Soc., Vol. 120, p. 9724-9725 (1998). In another embodiment, DNA can act as a nanoscopic switch to mediate charge transfer. DNA can be incorporated into a film as described in Okahata et al., J. Am. Chem. Soc., Vol. 120, p. 6165-6166 (1998). Redox matched switching elements can bind to or be activated by DNA.

One advantageous feature of nanoscopic switches is evident where the article is to be used as a sensor for detecting an analyte. In one embodiment, the nanoscopic switch can act as a site capable of detecting an analyte (e.g. a detection site), where the detecting step can involve a binding event between the analyte and the nanoscopic switch. For example, if the nanoscopic switch is part of the nanoscopic pathway, a binding even between the nanoscopic switch and the analyte can affect electronic properties of the nanoscopic switch and thus affect mediation properties. The present invention provides increased sensitivity in analyte detection due to the insulation of the nanoscopic pathway. Because the occurrence of a single binding can theoretically affect an entire nanoscopic pathway, (see FIG. 1), the occurrence of multiple binding events on multiple detection sites can have a great effect on the conductivity of the entire article, sometimes in a non-linear manner, thereby providing enhanced sensitivity. This contrasts with prior art sensors, in which detection sites are located within a near infinite number of conduction pathways. A binding event will affect the conductivity very minimally.

One embodiment provides a sensor comprising an article having a nanoscopic pathway. A theoretical example is provided by referring back to FIG. 1. For example, if nanoscopic switch 8 is in an "off" position (i.e., does not permit the transfer of electronic

charge) conduction cannot occur throughout pathway 4 in the direction of arrow 5. If the nanoscopic switch is capable of detecting an analyte, a binding event between the nanoscopic switch and the analyte will alter the electronic properties of the nanoscopic switch and allow at least some conduction to occur through pathway 4. Of course, this is one extreme

5   example, and the nanoscopic switch can alter conductivity simply by increasing or reducing conduction, for example, such as optimizing or decreasing an amount of orbital overlap between the nanoscopic switch and the pathway. In one embodiment, the sensor includes a plurality of nanoscopic pathways arranged in parallel to each other. Such an arrangement can provide the sensor with an increased signal.

10   Another aspect of the present invention provides a composition comprising a nanoscopic pathway and a polymer isolating the nanoscopic pathway. In one embodiment, the nanoscopic pathway is a conducting polymer, such as any conducting polymer disclosed herein. The polymer isolating the nanoscopic pathway can be a dielectric polymer, such as any dielectric polymer disclosed herein. In one embodiment, the composition comprises a

15   multi-stranded polymer. FIG. 2 schematically illustrates a multi-stranded polymer. In Fig. 2, the nanoscopic pathway is represented as a central conducting polymer. One or more dielectric polymers

In one embodiment, the dielectric polymer is attached to the conducting polymer. For certain examples, this attachment provides a rigidity that maintains the integrity of the

20   nanoscopic pathway, perhaps by preventing chain entanglement. The attachment can also be a result of the polymerization of a monomer having two polymerization sites (described below). In one embodiment, the dielectric polymer is attached to the conducting polymer via a chemical bond.

        One method for attaching a dielectric polymer to the conducting polymer is by

25   providing a structure comprising the formula:
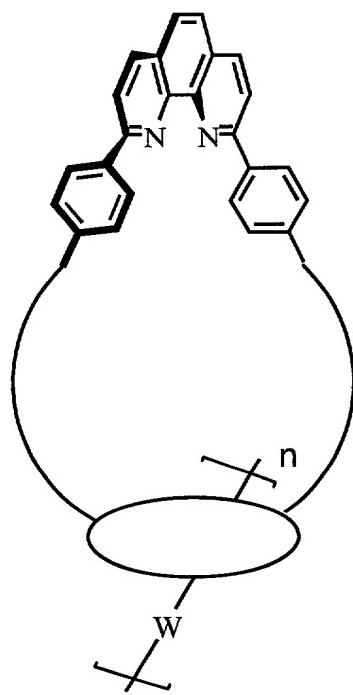
wherein $\Big(\ \ \Big)$ comprises two continuous chains of atoms and $\left[-W-\bigcirc-\right]_n$
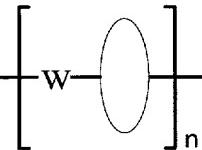
comprises a species which can be a dielectric or a conductive nanoscopic pathway, and n is

an integer greater than 0. Examples of such polymers can be found in FIG. 10. Those of

5   ordinary skill in the art can monomer of $\left[-W-\bigcirc-\right]_n$ to allow polymerization from one

or preferably two sites (or more) sites, as exemplified by the scheme of FIG. 10.

    Another aspect of the present invention provides a block co-polymer that can define a

nanoscopic pathway. In one embodiment, the block copolymer comprises blocks of a

conducting material and blocks of a dielectric material. In many instances, block copolymers

10   prefer to exist in a solid state phase in which "like" blocks separate into phases with "like"

blocks. This organization can create a microphase-separated block copolymer structure, as

schematically illustrated in FIG. 5. FIG. 5(a) schematically illustrates a conducting block

monomer 44 and a dielectric block monomer 46. FIG. 5(b) schematically illustrates a single

polymer chain 40 comprising a series of monomer blocks 44 alternating with a series of

15   dielectric blocks 46. FIG. 5(c) schematically illustrates the formation of a microphase-

separated structure 50, where regions 54 comprise an alignment of conducting blocks whereas regions 56 comprise an alignment of dielectric blocks. This structure provides an arrangement in which the conducting blocks allow conduction throughout an entire block (by conjugation, redox conductivity, or a combination thereof). In addition, the conducting

5   blocks are insulated by dielectric blocks. Depending upon the ratio of the compositions of each block the conducting block can be organized into layered structures or a hexagonal array of columns. The block copolymer can be a diblock, a triblock, or any multiblock copolymer as known in the art.

In one embodiment, dielectric blocks are selected from the group consisting of

10   polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof. In one embodiment, conducting blocks comprise conjugated organic groups, nanoparticles or a combination thereof. For example, the conducting blocks can be a conducting organic group, such as an organic group selected from the group

15   consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a conjugated ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof. The conducting block can comprise a gel.

Examples of block copolymers are presented in FIGs. 6-9.

20   FIG. 9 are examples of monomers in a polymer that can bind to metal ions or nanoparticles such as semiconductor nanoparticles.

In one embodiment, the activating step can involve redox-matching the nanoscopic pathway with the nanoscopic switch. In another embodiment, the activating comprises adjusting an electrochemical potential applied to the nanoscopic pathway. In these

25   embodiments, the nanoscopic switch is a part of the nanoscopic pathway.

Another aspect of the invention provides an article comprising a percolation network. A "percolation network" is a lattice comprising a random mixture of conducting and non-conducting links. A "percolation threshold" is a minimum concentration of conducting links necessary to generate a conduction pathway between two sites situated within the percolation

30   network. In one embodiment, the conducting links comprise sub-nanoscopic pathways in themselves, albeit of a smaller scale. Positioned amongst these sub-nanoscopic pathways are a plurality of nanoscopic switches which, when unactivated, are the non-conducting links.

The nanoscopic switches are capable of being activated such that they comprise a conducting link.

One example of this embodiment is schematically illustrated in FIG. 4. FIG. 4A schematically shows an article comprising nanoscopic particles 34 (sub-nanoscopic

5   pathways) and dielectric particles 36. Dielectric particles 36 can include nanoscopic switches 38. When none of nanoscopic switches 38 are activated, there exists no nanoscopic pathway between any of points A, B or C. When some of the nanoscopic switches are activated such as to allow mediation of conduction (e.g. components 38a-b), this concentration is sufficient to create a nanoscopic pathway between points A and C. Thus, the percolation threshold is

10 achieved.

In one embodiment, the nanoscopic switches can be activated by applying a defined electrochemical potential. In this embodiment, the nanoscopic switches are non-conducting within a first electrochemical potential range and conducting within an electrochemical potential range, the defined potential lying within that range.

15 In one embodiment, the nanoscopic switch is a metal ion. In another embodiment, the activating step involves changing a ligand environment around the metal ion. For example, the metal ion can be conducting when subjected to a first ligand environment and non-conducting when subjected to a second ligand environment.

In the embodiment where there is only one nanoscopic pathway, such as that

20 illustrated in FIG. 1, the conductivity is amplified via an on/off mechanism. In the embodiment where there are a number of nanoscopic pathways all contributing to the conductivity of the article, activation above the percolation threshold may involve establishing a some or all of the nanoscopic pathways, and thus amplifying involves an increase in the conductivity due to a greater number of nanoscopic pathways established.

25 Another aspect of the present invention provides a method for altering conductivity. The method involves providing an article comprising a nanoscopic pathway having a conductivity. The method further involves insulating the nanoscopic pathway and activating a nanoscopic switch positioned in the article. The activating step can involve: (1) Establishing electrical communication between one nanoscopic pathway and another

30 nanoscopic pathway, where the nanoscopic switch is positioned between two nanoscopic pathways, thereby producing a larger nanoscopic pathway; or (2) Redox-matching the nanoscopic pathway with the nanoscopic switch can result in optimal orbital overlap between

the two species, providing a more optimal conduction pathway. Redox-matching can be provided by any method described herein.

In one embodiment, the activating step involves applying an electrochemical potential to the nanoscopic pathway. This may be necessary where the nanoscopic pathway is

5   conducting within a particular electrochemical potential range.

Another aspect of the present invention provides a method for detecting the presence of an analyte. The method involves providing an article comprising a nanoscopic pathway having a conductivity and insulating the nanoscopic pathway. The method also involves activating detection sites positioned in the article.

10   In one embodiment, the activating comprises a binding event between the analyte and the detection site. In one embodiment, the binding event causes the detection site and the pathway to be redox-matched, thus increasing or reducing the extent of conduction in a detectable manner. In one embodiment, the detection site comprises a metal ion complex (e.g. a coordination compound, an organometallic compound). In one embodiment, the

15   analyte is a potential ligand which can bind to the metal ion of the complex. In another embodiment, the metal ion complex has a ligand which can bind other analyte ligands, either covalently, ionically, sterically (e.g. a cage or pseudo-cage). In one embodiment, the analyte is a metal ion and the metal ion complex has a ligand (e.g. a crown either, a macrocycle, etc.) which can bind the analyte metal ion.

20   In one embodiment, DNA comprises a detection site. The analyte can be any biological species capable of binding to DNA, such as a complementary strand of DNA or RNA.

Another aspect of the present invention provides a method for amplifying conductivity. The method involves providing an article comprising a nanoscopic pathway

25   and positioning a plurality of nanoscopic switches in the article. A number of the plurality of nanoscopic switches, the number being less than the total value of nanoscopic switches, is activated where the number is greater than a percolation threshold.

Another aspect of the invention a method for reducing conductivity. The method involves providing an article comprising a nanoscopic pathway and positioning a plurality of

30   nanoscopic switches in the article. In this aspect, a number of the plurality of nanoscopic switches is deactivated such that the number is less than a percolation threshold.

One aspect of the present invention provides a method for synthesizing a conducting

polymer. A monomer having first and second polymerization sites is provided. The method involves polymerizing the monomer at the first site to produce the first polymer. The monomer is then polymerized at the second site to produce the second polymer such that the second polymer insulates the first polymer. In one embodiment, the first polymer is a

5   conducting polymer of the types mentioned herein. The polymerization steps can occur either sequentially or simultaneously, so long as the second polymer is arranged to insulate the first polymer.

In one embodiment, the polymerization occurs by electropolymerization, i.e. by the application of a defined electrochemical potential. At this potential, the monomer undergoes

10   radical formation via reduction or oxidation (i.e. an electrochemical redox reaction), and recombination of these radicals produces oligomers. The oligomers are subsequently reduced or oxidized, and combined with other radical oligomers or monomers. In this embodiment, sequential polymerization can be effected by subjecting the monomer to a first electrochemical potential at which the first site undergoes an electrochemical redox reaction.

15   This potential, however, is not sufficiently large enough to initiate redox reactions at the second site. Upon completion of the first polymerization, the monomer is subjected to a greater electrochemical potential sufficient to cause redox reactions at the second site (see FIG. 10, for example). Other examples of this polymerization can be found in Marsella et al, J. Am. Chem. Soc., Vol. 116, p. 9346-8 (1994) and Marsella et al., J. Am. Chem. Soc., Vol.

20   117, p. 9832-9841 (1995), each of which is incorporated herein by reference in its entirety.

The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope

25   of the invention.

<u>Example 1</u>

Reactions were carried out in oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. ^{1}H NMR spectra were recorded with a Bruker AC-

30   250 or Varian Inova-500 MHz spectrometers. Electrochemical measurements were performed in an air-free dry-box using a computer controlled Autolab Model PGSTAT 20 potentiostat from Eco Chemie. All electrochemical measurements shown were performed on

interdigitated array microelectrodes purchased from AAI-ABTECH with an interelectrode spacing of 5 μm, with a platinum coil counter electrode and an isolated Ag wire quasi-reference electrode. All the potentials are reported versus the Fc/Fc$^+$ redox couple. Compound 6 was synthesized from the tosylate (Q. Zhou, T.M. Swager, *J. Am. Chem. Soc.*,

5   1995, 117, 12593) by simple exchange with iodide ion and 7 was produced synthesized as reported previously (C.O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron Lett.* 1983, 24, 5091). Macrocycle 64 was produced by straight forward adaptation of conditions used for the synthesis of related macrocycles (C.O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron Lett.* 1983, 24, 5091).

10   Additional experimental details can be found in a paper entitled "Three-Strand Conducting Ladder Polymers: Two-Step Electropolymerization of Metallorotaxanes", by J. Buey and T.M. Swager (*Angew. Chem. Int. Ed.* **2000**, *39, No. 3*, 608-612), which is herein incorporated by reference in its entirety.

15   Example 2

Synthesis of 63 (see FIG. 10): Compound 64 (100 mg, 0.115 mmol), 2-(tributylstannyl)-3,4 ethylenedioxythiophene (124 mg, 0.288 mmol), CuI (66 mg, 0.346 mmol) and t-PdCl$_2$(PPh$_3$)$_2$ (4 mg) were dissolved in 10 mL dry DMF and the mixture was stirred overnight at 80°C. The DMF was then evaporated and the residue was extracted with

20   CH$_2$Cl$_2$/NH$_4$OH. The organic phase was dried and the crude product was precipitated with hexane. Column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH 99:1) afforded the desired compound as a yellow solid in 90% yield.

                                       Example 3

25   Synthesis of Monomer 60 (see FIG. 10): A solution of [Cu(MeCN)$_4$] BF$_4$ (5.3 mg, 0.017 mmol) in dry deoxygenated MeCN (2 mL) was transferred via cannula to the solution of 62 (8 mg, 0.017 mmol) and 63 (15 mg, 0.017 mmol) in 10 mL dry deoxygenated dichloromethane. After 3 h stirring the solvents were evaporated and the residue was dissolved in acetone and filtered. Evaporation to small volume and addition of diethylether

30   afforded compound 60 as a green powder in 60% isolated yield.

Example 4

Synthesis of Monomer 61 (see FIG. 10): The synthesis was performed as described

for 60, using $Zn(ClO_4)_2$ $6H_2O$ (4.2 mg, 0.01 mmol), 62 (5.4 mg, 0.01 mmol) and 63 (10 mg,

0.01 mmol). Isolated yield 90% (orange solid).

5

Example 5

Synthesis of poly1, poly2, (see FIG. 10) and poly4: This example illustrates one

method for making an article of the present invention by sequentially polymerizing a

monomer having two polymerization sites. Synthesis of the 4,4'-bis(dithienyl)-2,2'-

10   bipyridine threading ligand 62 is prepared as described previously (see S.S. Zhu, T.M.

Swager, *Adv. Mater.* 1996, 8, 497) as well as its use for the formation of conducting

polymetallorotaxanes (see S.S. Zhu, T.M. Swager, *J. Am. Chem. Soc.* 1996, 118, 8713; S.S.

Zhu, T.M. Swager, *J. Am. Chem. Soc.* 1997, 119, 12568; P.L. Vidal, M. Billon, B. Divisia-

Blohorn, G. Bidan, J.M. Kern, J.-P. Sauvage, *Chem. Commun.* 1998, 629). The electron poor

15   nature of ligands requires a more positive oxidation potential to undergo

electropolymerization than would be required from an isolated bithiophene. To complement

this threading group, we designed and synthesized a new macrocycle, 63 (FIG. 10), bearing

an electron rich 1,4-bis(ethylenedioxythiophene)-2,5-dialkoxybenzene group that is easily

oxidatively polymerized at lower potentials. In accord with methods pioneered by Sauvage

20   and coworkers (J. C. Chambron, J.-P. Sauvage, *Chem. Eur. J.* 1998, 4, 1362; J.-P. Sauvage,

Acc. Chem. Res. 1998, 31, 611), simple mixing of 62, 63, and Cu^{1+} or Zn^{2+} ions produces

metallorotaxane monomers 60 and 61.

Controlled oxidation results in the electropolymerization of the macrocycle, 63, while

leaving the threading group 62 untouched. Higher potentials can be subsequently applied to

25   polymerize 62. The detailed procedure is as follows: Microelectrode arrays (G.P. Kittlesen,

H.S. White, M.S. Wrighton, *J. Am. Chem. Soc.* 1984, 106, 7389; J. W. Thackeray, H.S.

White, M.S. Wrighton, *J. Phys. Chem.* 1985, 89, 5133), are immersed in a solution (0.1 M n-

Bu_4NPF_6, CH_2Cl_2) of 60, 61, or 63 (0.3mM) and are cycled between -0.5 and 0.55 V vs.

Fc/Fc^+. This procedure results in the oxidative electropolymerization of the macrocycle to

30   produce poly1, poly2, (see FIG. 10) and poly4 (polymerization of 63 without metal ion). The

cyclic voltammetry data for the polymerization of 60 is shown in FIG. 11.

Cyclicvoltammetric analysis of poly2 in fresh monomer-free electrolyte gave

voltammograms indistinguishable from those obtained from poly4, as is consistent with polymerization. The cyclic voltammogram of poly1 (FIG. 11) is also similar but contains an added $Cu^{1+/2+}$ wave centered at 0.11V vs. Fc/Fc^+. The UV-vis spectra also supports the selective polymerization of the macrocyclic ligand, and both poly1 and poly2 displayed

5   absorption spectra similar to that of poly4 (λ_{max}= 503 nm) with an additional absorption feature at about 450 nm assigned to the threading ligand, 62.

Example 6

Synthesis of poly1-L and poly2-L (see FIG. 10): Subjecting deposited films of poly1

10   or poly2 to higher potentials in monomer-free electrolyte resulted in the polymerization of the 4,4'-bis(dithienyl)-2,2'-bipyridine threading ligand to form ladder polymers poly1-L and poly2-L, respectively. This process is readily apparent from FIG. 11 wherein the first sweep to 1 V vs. Fc/Fc^+ results in a large irreversible oxidation current. This irreversible current is expected since oxidation of the threading ligand, 62, will produce radical cations that undergo

15   intermolecular coupling with loss of protons to form new thiophene-thiophene linkages (i.e. polymerization). The second sweep over the same expanded potential range lacks this irreversible oxidation and is identical to all subsequent sweeps.

The efficiency of the second polymerization can be deduced from an analysis of the irreversible charge relative to the reversible charge. A key parameter is the mass of the

20   polymer immobilized on the electrodes. Once the mass of the polymer has been determined, the degree of oxidation of the polymer is also known. This analysis was afforded by a comparison of poly1, poly2, and poly4. Due to the fact that the metal ions do not directly interact with the macrocyclic polymer's electronic structure, poly2 and poly4 have nearly identical cyclic voltammetric responses over the potential region of –0.5-0.55 V vs. Fc/Fc^+

25   and display the same number of Coulombs per gram of polymer deposited. Poly1 has an additional one electron $Cu^{1+/2+}$ wave in that potential region, which also serves as an internal standard to establish the moles of polymer repeating units in the film.

It can be seen that poly1, poly2, and poly4 are respectively oxidized by 3.2, 2.2, and 2.2 electron per repeating unit when cycled to 0.55 V vs. Fc/Fc^+. With regard to the

30   efficiency of the second polymerization of poly1 and poly2, the respective irreversible charge passed was 1.7 and 2.1 electron per repeating group. A quantitative polymerization results in 2 electrons per monomer being removed irreversibly. After the first sweep to high potential a

stable reproducible voltammogram is observed and with application of 0.98 V vs. Fc/Fc^+ 5.3, 5.4, and 3.3 electrons per repeating unit were removed for poly1-L, poly2-L and poly4, respectively. For a perfect structure it would be expected that poly1-L, due to the presence of Cu ion, would be oxidized by one more electron than poly2-L. The smaller value for poly1-L

5   reflects the concurrent loss of 62 and the Cu ion.

The linear dimensions of the two polymerizable groups and the structure of the metallorotaxane were chosen to promote the formation of a three-stranded ladder polymer (FIG. 10). Neglecting minor effects arising from conformational issues (there are two enantiomeric conformations of 60 and 61) the polymer formed from the threading unit is

10   twice as long as the polymer containing the macrocycle. Additionally, computationally optimized structures (All calculations were performed with the Spartan program (Wave-function, Inc.).

The geometry of 60 was optimized using semiemperical calculations (PM3). The structure of the octamer was minimized by molecular mechanics (MMFF94). Analysis of

15   the monomers indicates that the two polymerizable groups are rigidly held in a parallel orientation. These structural features and the polymerization of the threading ligand require the structure of the polymer to contain a predominance of the three-stranded ladder architecture shown in FIG. 10. This ladder polymer structure is of particular interest due to the fact that the macrocyclic-containing polymer (poly4) is sandwiched between two chains

20   for poly3. Thus, a three-stranded molecular wire has been assembled in which the internal wire is encapsulated between two polymer chains.

To further illustrate the viability of this structure, molecular mechanics calculations were conducted on oligomers assembled from the computationally optimized monomer. (All calculations were performed with the Spartan program (Wave-function, Inc.). FIG. 21 shows

25   a space-filling model of 60 (a) and an octamer of poly1-L (b). In FIG. 21(a), the backbone of poly4 is shown as the medium-shaded portion, the light-shaded portion represents the phenanthroline portion, and the dark-shaded portion represents the poly3 chains. Corresponding Fig. 21(b) shows the backbone of poly4 as the middle polymer sandwiched between poly3 chains. The geometry of 60 was optimized using semiemperical calculations

30   (PM3). The structure of the octamer was minimized by molecular mechanics (MMFF94).)
In these calculations a single enantiomer of 60 was used. As can be seen from the space filling structure of the octamer shown in FIG. 21, a corresponding polymer would show a

clear match of the polymer lengths, and the chain of poly4 is incarcerated between two

strands of poly3. An additional feature revealed by the structure is the steric constraints of

the phenanthroline portion of the macrocycle. This unit presents a rigid steric barrier that

prevents close contacts between neighboring polymers and thereby promotes intrapolymer

5   coupling in the second polymerization to favor the three-strand ladder structure.

Comparisons of the conductivity and electrochemistry (FIG. 12) of poly1-L, poly2-L,

and poly4 provide evidence that the internal polymer behaves as a partially isolated wire

when the outer two polymer-strands are in their insulating (undoped) state. The observed

electroactivity has three components; (1) the macrocyclic polymer, (2) the Cu center (for

10   poly1-L), and (3) the threading polymer. A comparison with poly4 (FIG. 12) indicates that

the first wave at about $0.1V$ vs. Fc/Fc^+ and a broad featureless electroactivity at more positive

potentials for poly1-L and poly2-L can be assigned to the macrocycle-containing polymer.

For poly1-L the $Cu^{1+/2+}$ wave overlaps the macrocyclic polymer's electroactivity, which

creates an optimal situation for the Cu-centered electroactivity to enhance the conductivity.

15   The conductivities of rotaxane complexes of poly3 have been previously determined

to be low (ca. 10^{-3} S/cm), and thus the poly4 backbone is the dominant contributor to the

conductivity of the ladder polymers. Simple inspection of FIG. 21 reveals that the

conductivity (σ) of poly1-L (to obtain conductivities the coverage on the electrodes were

determined by profilometry and are related to the conductivity of poly(3-methylthiophene),

20    $\sigma = 60$ S cm^{-1} to correct for non-uniform coverage – this method has been established to

provide a reliable measurement of a number of electropolymerizable monomers. R.P.

Kingsborough, T.M. Swager, *Adv. Mater.* 1998, 10,1100; G. Zotti, G. Schiavon, *Synth. Met.*

1990, 39, 183; G. Schiavon, S. Sitran, G. Zotti, *Synth. Met.* 1989, 32, 209) at 0.25 V vs.

Fc/Fc^+ is 38 S/cm^{-1}), is approximately 20 times higher that poly2-L at the same potential ($\sigma =$

25   2 S/cm). Likewise, the conductivity of poly4 at the same potential is 66 S/cm^{-1}. All three

materials poly1-L, poly2-L, and poly4 display comparable (within a factor of 2)

conductivities at high potentials ($\sim$ 0.9 V vs. Fc/Fc^+). These conductivity comparisons

demonstrate that the central macrocyclic polymer (poly4) in poly1-L and poly2-L is isolated

by the outer polymers (poly3 chains) when they are in their insulating states. When the

30   poly3 chains are insulating, the Cu ion's electroactivity can assist in interchain transport. The

Cu ion's redox potential is optimally positioned to participate in the conduction. This effect,

illustrated in FIG. 13 (poly3 chains comprising macrocycle 70 and chain 72 and poly4 chain

indicated by 74), is responsible for the much larger conductivity at lower potentials of poly1-L relative to poly2-L. In the absence of a rotaxane structure the polymer chains of poly3 can come in close proximity, and poly4 exhibits a high conductivity without the Cu-centered electroactivity. At higher potentials the poly3 chains are redox active and mediate interchain

5   conduction. Hence, there exists similar conductivities for poly1-L, poly2-L, and poly4.

Example 7

The synthesis of the iptycene-containing phthalocyanine monomers is shown in FIG. 14. Quinone 1 is converted to 2 by reaction with bromine in chloroform. Reduction of the

10   quinone 2 to the hydroquinone 3 is carried out using $Na_2S_2O_4$ in a biphasic Et_2O/H_2O solvent system. Alkylation of the hydroquinone 3 affords 4 in high yields. Cyanation of 4 with CuCN in DMF yields the dicyano derivative 5 in moderate yields. Conversion diiminoisoindoline (6) is carried out by bubbling ammonia through a suspension of 5 in ethylene glycol at 140 °C with a catalytic amount of Na for 5 h. Compound 6 (A) is then

15   cyclized with 4-iodophthalonitrile (S.M. Marcuccio, P.I. Svirskaya, S. Greenberg, A.B.P. Lever, C. Leznoff, K.B. Tomer, *Can. J. Chem.* 1985, 63, 3057), (B) in a refluxing $Mg(OBu)_2$ suspension in BuOH. After trifluoroacetic acid treatment, the free bases of the three isomers, $2H[pz(A_3;B)]$, cis-$2H[pz(A_2;B_2)]$, and $trans$-$2H[pz(A_2;B_2)]$, are obtained. Subsequently, the crude mixture is metallated with $M(acac)_2$ in refluxing THF (M = Co, Ni). The crude

20   metallophthalocyanine mixture is then reacted with 2-tributylstannyl-3,4-ethylenedioxythiophene in DMF at 60 °C in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$. Separation of the three isomers, 7-Co, 8-Co, and 9-Co, (or 7-Ni, 8-Ni, and 9-Ni) is easily accomplished by flash chromatography. The alternating mixed ring phthalocyanines (precursors to 9-Co and 9-Ni) are the major products. Compounds 7-Co and

25   7-Ni with a single thiophene group are incapable of forming polymers and were not studied further. CPK space-filling models indicate that the iptycene architecture should create a pocket at the metal center.

Example 8

30   The electrochemical characteristics of both the *cis* and *trans* isomers and their polymers were investigated. Electropolymerization of 9-Co and 9-Ni on 2 μm interdigitated microelectrodes (G.P. Kittlesen, H.S. White, M.S. Wrighton, *J. Am. Chem. Soc.* 1984, 106,

7389; E.W. Paul, A.J. Ricco, M.S. Wrighton, *J. Phys. Chem.* 1985, 89, 1441; J.W.

Thackeray, H.S. White, M.S. Wrighton, *J. Phys. Chem.* 1985, 89, 5133; D. Ofer, R.M.

Crooks, M.S. Wrighton, *J. Am. Chem. Soc.* 1990, 112, 7869), results in the deposition of dark

green films of poly(9-Co) and poly(9-Ni). The polymerization proceeds by oxidative

5   coupling of the pendant thiophenes (FIG. 14). The cyclic voltammogram of these polymers

in fresh (monomer free) electrolyte on the interdigitated microelectrodes (Pt button electrodes

give identical results) is shown in FIG. 15a. Films of poly(9-Co) are characterized by a

wave at -0.6 V vs Fc/Fc$^+$ (Unless noted all potentials are referenced to the Fc/Fc$^+$ redox

couple), which is attributed to the Co$^{1+/2+}$ redox process, followed by a very broad region of

10   redox activity. This broad nature suggests overlapping or admixed redox processes (i.e.

redox matched), including the Co$^{2+/3+}$ redox wave, a ligand-based oxidation, and EDOT-

based electrochemistry. The conductivity profile is observed to increase at potentials

corresponding to the Co$^{2+/3+}$ redox wave, suggesting that the metal centered redox activity

contributes to the conductivity, and finally reaches a maximum at 0.35 V. The low hysteresis

15   in the conductivity and voltammogram suggests that minimal structural reorganization

accompanies the redox cycling. Using methods described previously (R.P. Kingsborough,

T.M. Swager, *Adv. Mater.* 1998, 10, 1003; R.P. Kingsborough, T.M. Swager, *J. Am. Chem.*

Soc. 1999, 121, 8825), a maximum conductivity of approximately 40 S/cm is obtained.

    Poly(9-Ni) displays new features in the reductive region at -1.35 V and -1.75 V (FIG.

20   15b). Based upon comparisons of cyclic voltammograms with those of the *cis* derivative, 8-

Ni, the first one-electron wave is assigned to a Ni$^{1+/2+}$ redox process and the second to a

ligand-centered process. In the oxidative region, the cyclic voltammogram of poly(9-Ni)

consists of a single broad redox wave centered at 0.3 V with a leading shoulder at 0.1 V. The

higher oxidation potential required for electroactivity of poly(9-Ni) compared to poly(9-Co)

25   is not unexpected since it lacks the lower potential Co$^{1+/2+}$ and Co$^{2+/3+}$ redox waves. The *in*

situ conductivity trace (FIG. 15b) shows redox conduction associated only with the polymer

backbone and not the metal-centered and ligand-centered reductive processes. The Co$^{1+/2+}$

wave, which is not redox-matched, produces no conductivity in poly(9-Co). The maximum

conductivity is observed at the half-wave potential of the polymer film (σ_{max} = 30 S/cm) and

30   decreases rapidly at higher applied potentials.

Example 9

Films of poly(8-Co) were also investigated with 2 μm interdigitated microelectrodes, and the cyclic voltammogram is shown in FIG. 16. FIG. 16 shows a large oxidation current followed by a plateau region, which is indicative of a highly delocalized polymer backbone.

5 This plateau region in the CV includes the overlapping electrochemical $Co^{2+/3+}$, ligand oxidation, and polymer oxidation processes. After reversal of the potential sweep at 0.5 V, a pronounced hysteresis is observed in the reduction wave and conductivity profile. Upon polymer oxidation, the in situ conductivity profile rapidly increases and levels off on a plateau conductivity of ca. 55 S/cm. The hysteresis and high conductivity suggests that the

10 cis-geometry favors greater interchain interactions in the oxidized polymer.

Example 10

This example presents another approach to design monomers that can be both electropolymerized and cyclized in a tandem process. Thiophene groups can be attached in

15 one of two fashions, either through the position α or β to the sulfur. In the first case cyclization as shown (top) in FIG. 17 proceeds through the less reactive β—position and the polymerization can occur through the α—position. In this polymer the only conjugation path involves the phenyl ring resulting in a higher band-gap and higher oxidation potential. In the case shown (bottom) in FIG. 17 the cyclization and polymerization both occur through

20 the more reactive α—positions. A conjugation path exists through the thiophene residues and these systems are easier to oxidize and have lower band gaps.

Different R groups can be used where R = CH_3, OCH_3, H, crown ethers. The cyclic voltammetric behaviors of the film-growth (polymerization) and of the polymer film are shown in FIG. 18 for β-linked monomers. FIG. 18 shows electropolymerization (a) of the

25 monomer: The dashed line is the first sweep and the increasing current with successive sweeps indicates that polymerization occurs; the cyclic voltammetric behavior of the thin film (b) on a 2 mm^2 platinum button electrode shows reversible electrochemical behavior, (scan rates were 100m V/s) This material shows both excellent growth characteristics and electroactivity. The cyclic voltammetric behavior suggests that this film is highly conductive.

30 The films have excellent durability and can be cycled many (10^3 +) times over the potential range shown without degradation. The films can be cycled to higher potentials vs. Ag/Ag^+ in acetonitrile solutions and degrade at potentials around 2 volts, potentials whereat the solvent

is also degrading. These films can be stable in aqueous media, a feature relevant to ascertain stability in ambient conditions. The crown ether linkages bind metal ions and change the redox potential of segments of the polymer and thereby constitute a switching mechanism.

The β–linked tetrathienyl monomer of FIG. 19 displays very desirable

5   electrochemical behavior and is readily electropolymerized into thin highly conductive films. The added solubility of the hexyl sidechains can make soluble analogs. The α–linked monomer undergoes an irreversible oxidation at 0.9 V vs. Ag/Ag$^+$ suggestive of a cyclization and/or polymerization. Due to the higher solubility no film deposition was observed. The model compound displays reversible redox wave in CH_2Cl_2 electrolyte at $E^{1/2}$= 1.25 V vs.

10   Ag/A.

Example 11

Electron-rich macrocyclic monomers can be polymerized about electron-poor template polymers as shown in FIG. 20. Polyrotaxane 82 can be produced by either

15   polymerizing rotaxane monomer (pathway A, comprising electron rich macrocycle 80 and electron poor templating polymer 81) or by assembling macrocycle 80 around an existing templating polymer 81. In the simplest case, the macrocycle 80 will have coupling sites 80a and 80b and polymers with structures schematically shown as 83 or 84 will be formed. This polymer is a ladder polymer by virtue of the fact that to completely sever the polymer

20   backbone two bonds must be broken. However the strong covalent bonds are on two different polymers held together by non-covalent interactions. Few such synthetic ladder polymers have been previously synthesized. Non-covalent ladder polymers in biological species and related assemblies can also be used (e.g. DNA, beta-sheets). Macrocycles containing four coupling sites can create three strand ladder polymers 84.

25   Monomer 90 can function as the electron poor element. This choice is based upon the fact that the diol structure is readily converted to a number of polymeric structures (e.g. polyesters, polysiloxanes, etc.) by standard methods. Great flexibility can be provided in the choice of a linking group. Linking groups that can be readily cleaved will allow for the electron poor templating polymer to be removed. Removal of the template in 84 can generate

30   a tubular structure which can be subsequently utilized for the transport/binding of ions or small molecules to produce separation/sensory materials. Furthermore the binding of

polymerizable monomers by 84 can be used to organize dielectric polymers and isolate 84 to produce a nanoscopic pathway.

The reactive groups used to interconnect the macrocycles can similarly be varied. Oxidative polymerization of electron-rich heterocyclic monomers is one process for the

5   synthesis of conducting polymers. This polymerization can also allow for electro-deposition directly onto devices and substrates for physical measurements. The syntheses of electron-rich macrocyclic monomers 93-96 can result in assembly into polyrotaxanes when mixed with 90 or related materials. Once assembled into a polyrotaxane complex, oxidation can form oligothiophene interconnects to produce the ladder structure. Structures 93 and 94 will

10   lead to ladder polymers of structure 83 and monomers 95 and 96 will produce structure 84.

Polymer 92 can also be used as a conjugated polymer template. Polymer 92, a very electron-poor polymer previously synthesized (Marsella et. al. *Advanced Materials* 7, 145-147, 1995), is an efficient threading element for the formation of polyrotaxane complexes. The resultant ladder polymers will have electron-rich and electron-poor polymers with close

15   co-facial contacts. Photoexcititation will transfer an electron to 92 from the macrocycle containing polymer, and the conjugated nature of both polymers will allow for the carriers to rapidly diffuse away from each other and hence produce long lived charge separation. This charge separation should produce an accompanying photocurrent when placed between two electrodes in an electric field.

20

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be examples and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that,

25   within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described.

What is claimed: